ASPHALENE SELF-ASSOCIATION -
A COMPUTER SIMULATION STUDY

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INTRODUCTION

Self-association of asphaltenes and the resulting colloidal-like particle structure, polydispersity, and other physical properties have drawn great scientific attention in the past decade. They are relevant to oil production, transportation and refining. One key question is yet to be answered is the energies that are involved in the self-association process. From thermodynamical point of view, the conventional micellization process is mainly driven by the hydrophilicity-hydrophobicity imbalance. Other energies, such as packing, double layer interacting, etc., often play minor roles only. The self-association of asphaltenes appear to be very different. Asphaltenes are defined based on the solubility. Their molecular structures are not unique. The molecules often consist of various degree of polynuclear aromaticity. No distinctive hydrophilic and hydrophobic portions in the molecules can be identified. Additionally, asphaltenes only self-associate in the organic environment with low permmittivities. This amounts to saying that the hydrophilicity-hydrophobicity imbalance should not be the governing factor, and that the interactions between molecules are short ranged. In the past decade, experiments, theories and computer simulations have been reported on this issue [1-3]. Good progress has been made, however, the fundamental understanding of the self-association mechanism is still lacking.

In this study, we performed a molecular dynamic simulation to study the self-association process. The aim is to identify the governing energy in this association process. One difficulty in this simulation is to mimic the real systems. It requires in-depth knowledge of the system. In our case, we chose the Ratawi vacuum residue (VR) derived asphaltene as the system. Ratawi VR asphaltene have been well studied in our laboratory. Data regarding its elemental analysis, chemical properties, and physical properties are readily available for us to construct the molecular structures, distribution and the initial configuration of the simulation.

COMPUTATIONAL DETAIL

The simulation consists of 64 asphaltene molecules ranging in size from 3 rings to 11 rings structure. The ring distribution was based on the Gaussian distribution with the peak at the 7 ring structure [4]. Two systems were modeled. One at a concentration of 0.015 wt % (below the critical micelle concentration, CMC) and the other at 5 wt % (above CMC). The size of the cell was chosen to represent the system at the desired densities. With the above concentrations, the corresponding cell dimensions are 743.0 Å and 108.8 Å respectively. The molecular dynamic (MD) simulation was performed using CERIUS2 [5]. The molecules were placed randomly in the cell using the amorphous cell module in the Cerius2 package to define the initial configuration. This was followed by energy minimization. During the energy minimization process, the Dreiding force field was used to account for

both inter- and intra-molecular interactions except the electrostatic ones [6]. A dielectric continuum of 3.5 was used to model the solvent. Dreiding Force field was not used to compute the electrostatic interactions because it calculates the monopole-monopole interactions only. One can still use the Dreiding Force field for computing electrostatic interactions, provided the monopole-monopole interactions calculated can represent a good estimate of the intramolecular dipole moments. We tested several computation packages on this issue. We used charge equilibration, MOPAC6 [7], and CHARMM [8] to compute the electrostatic interations, then evaluate the dipole moments estimated and compared with the experimental values. Single ring and double ring molecules as the test cases. MOPAC6 was found to be far superior to the other two packages as far as dipole moment representation is concerned. We thus calculated the electrostatic charges using MOPAC6. The MD simulation was lasted for 250 picoseconds (ps) where the system energy starts to be stable.

RESULTS AND CONCLUSION

Figure 1 and 2 show the simulation results for the 0.015 wt % and 5 wt % respectively. As one can see, the 0.015 wt % does not show significant self-association. Dimers do exist, but no large aggregates are observed. On the other hand, the 5 wt % shows aggregates of various sizes. F (see figure 2) is a small aggregate while B, C, D and E are large ones of different shapes. Their common feature is the short range stacking phenomenon. The maximum stack observed contains approximately 7 asphaltene molecules. This was predicted by Yen based on the solid phase compounds. In solvent, these stacks appears to preserve. However, the stacks are loose and somewhat irregular (see D in figure 2). Aggregate B is a good example. It consists of many short range stacks linked loosely together. As a result the aggregate does not show well defined cylindrical shape. It appears more like a sphere. This is also true for aggregate A, C and E. Aggregate D is more like a cylinder although the stacking direction changes after 7th molecules. We also found a monomer in this simulation (unmarked molecule in Figure 2) which may or may not be significant. In order to evaluate the importance of the dipole-dipole interaction, we used the charges obtained from charge equilibration method to compute the electrostatic contribution, which under estimate the dipole moments for simple molecules. The result shows a collapse of the molecules into a single huge aggregate. Since experimental data from small angle neutron scattering (SANS) and small angle X-ray scattering (SAXS) [1,9] have indicated the average size of the aggregates to be approximately 30 ?, the occurrence of a collapse single aggregate phase should not be the case. This indicates, at least indirectly, that dipole-dipole interaction must play an important role in controlling the self-association process.

From the nucleation process point of view a system can undergo nucleation only when the dipole moment of the system is zero. If a non-zero dipole moment is introduced, the nucleation process would be terminated at a some point and the nucleation process would not be complete. This seems to be the case in asphaltene self-association process. The self-association of asphaltenes can be viewed as a nucleation process. It is initiated when concentration exceeds the CMC [9]. At the beginning stage, the molecules stack to form cylindrical-like aggregates. This process is then terminated partially due to non-homogeneous molecular structures which makes the

stacks loose, but mainly due to non-zero dipole-dipole interactions. As a result, the phase separation occurs only at microscopic length scale, similar to a micelle solution, though the energies involved are completely different. The dipole moments can arise from the structural arrangement of the atoms in the molecules and the heteroatoms (Nitrogen, sulfur, nickel, vanadium etc.) that are commonly found in asphaltenes.

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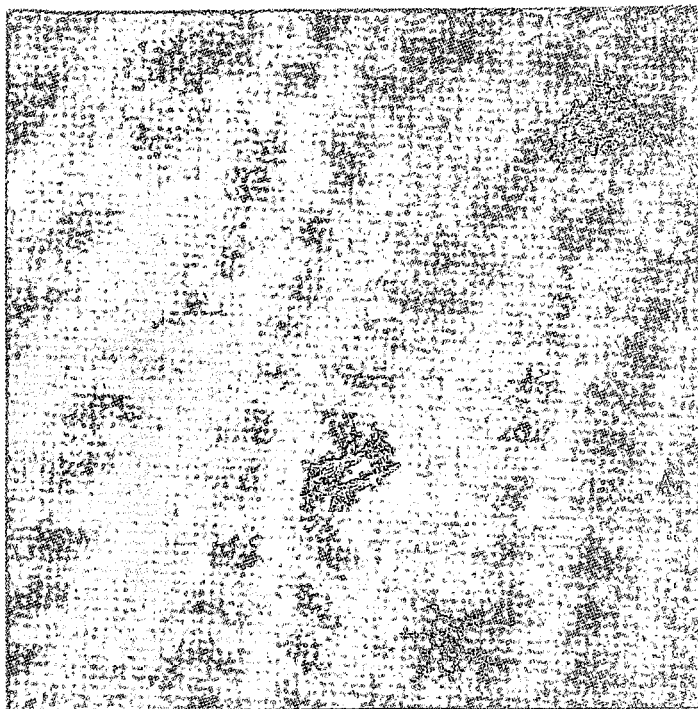[9] E. Y. Sheu, J. Phys. : Condens. Matter 8, A125 (1996).

Figure 1. MD simulation for 0.015 wt % Ratawi Aphaltene in solvent.

Figure 2. MD simulation for 5.0 wt % Ratawi Aphaltene in solvent.